⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 135 475**
A1

⑫

EUROPEAN PATENT APPLICATION

㉑ Application number: **84810391.7**

㉒ Date of filing: **08.08.84**

(51) Int. Cl.^{4}: **C 25 B 11/06**
C 25 C 7/02

㉚ Priority: **18.08.83 EP 83810368**

㊸ Date of publication of application:
27.03.85 Bulletin 85/13

㉞ Designated Contracting States:
AT BE DE FR GB IT NL SE

㊆ Applicant: **ELTECH SYSTEMS CORPORATION**
Corporate Headquaters 6100 Glades Road/Suite 305
Boca Raton Florida 33434(US)

㊇ Inventor: **Hinden, Jean**
chemin de la Fontaine 40
CH-1292 Chambésy(CH)

㊇ Inventor: **Waeffler, Jean-Pierre**
47 Chemin Saussac
CH-1256 Troinex(CH)

㊇ Inventor: **Katz, Michael**
48 Horerstrasse
IL-Haifa 34342(IL)

㊉ Representative: **Faltas Mikhail, William et al,**
ELTECH SYSTEMS CORPORATION 17-19, chemin du
Champ d'Anier
CH-1209 Petit-Saconnex (Genève)(CH)

㊹ **Manufacture of oxygen evolving anodes with film forming metal base and catalytic oxide coating comprising ruthenium.**

㊼ The invention provides a method of manufacturing dimensionally stable oxygen evolving anodes with a titanium base and a catalytic oxide coating which is produced from a coating solution containing Ru and Mn compounds in concentrations corresponding to a mole ratio of RuO_2 to MnO_2 from 1:1 to 1:9. The solution is applied and dried, followed by heat treatment in air at 400°C, so as to produce an oxide coating in 6 to 35 layers with a total loading of Ru = 4 to 20 g/m^2. Accelerated testing in sulphuric acid of anodes manufactured within these ranges shows a low oxygen potential during prolonged operation as an oxygen evolving anode.

Croydon Printing Company Ltd.

MANUFACTURE OF OXYGEN EVOLVING ANODES WITH FILM-FORMING METAL BASE AND CATALYTIC OXIDE COATING COMPRISING RUTHENIUM

FIELD OF THE INVENTION

The present invention generally relates to catalytic oxygen evolving anodes, and more particularly to a method of manufacturing a dimensionally stable, oxygen evolving anode which comprises an anode base of film-forming metal with a catalytic oxide coating containing ruthenium, and which may be applied for example in processes for electrowinning metals from acid electrolytes.

BACKGROUND ART

Oxygen evolving anodes are subject to particularly severe oxidative attack and corrosion due to anodically evolved oxygen and corrosive electrolytes. An industrially acceptable oxygen evolving anode must thus be adequately protected from oxidation by anodically evolved oxygen, in order to be able to ensure stable operation and a sufficiently long industrial service life to allow the anode cost to be economically justified for industrial applications of oxygen evolving anodes.

Metal electrowinning cells are generally operated with a low current density in order to ensure uniform electrodeposition of metal on the cathode, and thus require a very large anode surface area. The value of the metal product obtained on the cathode is moreover relatively low with respect to the area of the electrodes, so that the anode cost is particularly critical and must be restricted accordingly, so as to be economically justified for electrowinning.

Lead or lead alloy anodes have been widely used in processes for electrowinning metals from sulphate solutions, but they nevertheless have important limitations, such as a high oxygen overvoltage and loss of the anode material leading to contamination of the metal product obtained on the cathode.

Anodes of lead-silver alloy provide a certain decrease of the oxygen overvoltage and improvement of the current efficiency, but they still have the said limitations as a whole.

Known titanium anodes with an outer coating of manganese dioxide or lead dioxide have a high oxygen overpotential and do not provide an adequate energy economy and long-term service life to justify their use in most industrial applications of oxygen evolving anodes, and more particularly where conventional lead anodes are currently used.

It has been proposed to provide coated titanium anodes with a protective intermediate comprising platinum group metal, but this is nevertheless insufficient to provide an adequate service life for most industrial applications of oxygen evolving anodes.

It has also been proposed to provide dimensionally stable titanium anodes with a catalytic oxide coating for oxygen evolution at a reduced potential in order to achieve significant energy savings, while at the same time serving to protect the titanium base from anodic oxidation. The relatively high cost of most of the proposed oxygen evolving anodes, their limited industrial long-term service life, or both, nevertheless generally constitute major obstacles to their widespread use for most industrial applications.

The main problem in this connection, is that on one hand the severe oxidative attack under the very harsh operating conditions of oxygen evolving anodes, and on the other hand their extremely severe economic restrictions, make it particularly difficult to maintain high, long-term catalytic activity and ensure a low oxygen potential for a sufficiently extended period to allow the costs of using a catalytic anode to be justified by the total energy savings it provides during its useful service life.

Since no single material can by itself meet the requirements of an oxygen evolving anode, different anode materials must be combined in a suitable manner in order to allow these requirements to be met as far as possible. The selection of suitable anode materials is evidently important in this connection, and a broad variety of materials has been proposed for this purpose. The manner in which different anode materials are combined is neverthelsess particularly critical for the production of a consolidated operative anode structure which is suitable for operation as an oxygen evolving anode.

Titanium is a film-forming metal which exhibits outstanding corrosion resistance under anodic operating conditions, due to its ability to anodically form a stable surface oxide film which effectively protects the underlying titanium metal from corrosion, but is electrically insulating.

Dimensionally stable anodes thus generally comprise a titanium base provided with a catalytic coating which allows anode operation at a reduced potential and at the same time protects the underlying titanium from oxidation. On the other hand, any part of the titanium base which is exposed to the electrolyte is rapidly passivated and thus effectively protected by localized formation of a stable, insulating anodic surface oxide film on the part thus exposed.

In order to provide an operative anode structure, the catalytic coating must be permanently applied and electrically connected to the titanium base, and must itself exhibit adequate conductivity, catalytic activity, and stabilty to be able to ensure satisfactory, stable, long-term industrial operation of the anode. For this purpose, suitable anode coating materials must be selected and applied in a suitable manner to the anode base.

It is known that ruthenium provides excellent catalytic activity for oxygen evolution, but lacks adequate stability and tends to form volatile RuO_4 under oxygen evolving conditions. Consequently, ruthenium must be applied and stabilized in a suitable manner in order to allow it to effectively catalyze oxygen evolution at a reduced potential for prolonged periods. This constitutes a particularly critical technical problem underlying the present invention.

Ruthenium was for the first time successfully applied by H.Beer to produce dimensionally stable chlorine anodes with a mixed oxide coating of the type described more particularly in Example 1 of in U.S. Pat. 3,632,498, which combines the high stability of rutile TiO_2 with the excellent electrocatalytic properties of RuO_2 for chlorine evolution. Said mixed oxide at the same time provides an increased oxygen potential, and thereby increases the selectivity of the coating for producing chlorine as opposed to oxygen.

These significant advantages and more particularly the high stability of such anodes explain their outstanding success in the chlorine industry throughout the world since many years.

Such an anode with a TiO_2-RuO_2 mixed oxide coating nevertheless seems unsuitable for most applications of oxygen evolving anodes.

The development of an industrially acceptable catalytic anode for a given application involves complex problems since the industrial performance of an anode depends on numerous intricately linked and interacting factors such as, for example: the choice of anode materials, its manufacturing process and conditions, the industrial application and operating conditions of the anode.

While a multitude of patents reflect on one hand the great interest and considerable efforts to develop catalytic anodes, it is quite remarkable that only very few anode embodiments are on the other hand industrially applied on a large scale. This striking discrepancy between innumerable anodes proposed and the very few embodiments actually applied in practice is nevertheless not so surprising in light of the complex problems and interacting factors, which make any attempt to develop an anode that fully meets the extremely severe technical and economic industrial requirements a particularly difficult and unpredictable undertaking.

The state of the art relating to anodes of film-forming metal with a catalytic oxide coating comprising a precious metal oxide and manganese oxide may be illustrated by U.S. Patent No. 4,052,271. Example 8 of this patent relates to a titanium anode with a coating comprising iridium oxide and manganese oxide. This anode is said to be suited for the preparation of per-compounds, thus presumably has a relatively high oxygen potential for this purpose, and would for that reason seem unsuitable for most industrial applications of oxygen evolving anodes.

U.S. Patent No. 4,289,591 relates to a method of generating oxygen which comprises providing a catalytic cathode and a catalytic oxygen evolving anode respectively bonded to opposite surfaces of a solid polymer electrolyte ion transporting membrane, a catalyst comprising ruthenium oxide and manganese oxide being provided at the anode. This catalyst is produced by a modified Adams method which comprises mixing ruthenium and manganese salts, incorporating an excess of sodium nitrate, fusing the mixture at 500°C for three hours, washing and drying the residue to provide ruthenium oxide-manganese oxide powder, which is then bonded to said solid polymer electrolyte ion transport membrane. The described modified Adams method serves to produce a finely divided catalyst powder which is formed of a solid solution of ruthenium oxide with a minor amount of manganese oxide, and is bonded to said solid polymer electrolyte membrane. Such a composite membrane/electrode structure is nevertheless unsuitable for electrolytic processes such as electrowinning zinc or copper for example, which involve no separation by a membrane between the anodes and the cathodes.

It is well known to those skilled in the art that the manufacture of a complete, operative anode structure having a catalytic oxide coating consolidated with a film-forming metal base is quite problematic and that very slight modifications in the manufacturing conditions can drastically affect anode performance in industrial practice.

It is known that catalytic anodes comprising ruthenium undergo a notable rise in the oxygen potential during operation as oxygen evolving anodes. This constitutes a major obstacle to the effective use of the excellent electrocatalytic properties of ruthenium in oxygen evolving anodes, which is a major problem underlying the present invention.

DISCLOSURE OF THE INVENTION

A main object of the invention is to allow dimensionally stable, oxygen evolving anodes which comprises an anode base of film-forming metal with a catalytic oxide coating containing ruthenium to be produced in a simple and economical manner.

Another object of the invention is to provide a method of manufacturing such dimensionally stable anodes which allows ruthenium to be applied as efficiently as possible to maintain a reduced potential, significant energy savings, and an extended service life as an oxygen evolving anode.

A further object of the invention is to manufacture such dimensionally stable anodes which may be applied more particularly as oxygen evolving anodes in processes for electrowinning metals from acid electrolytes.

The invention provides the manufacturing method set forth in the claims with a view to meeting the above objects as far as possible.

It has been experimentally established that an oxygen evolving anode according to the invention must comprise a minimum proportion of manganese in order to be able to ensure an adequate anode life under oxygen evolving conditions.

It has been established in this connection that the coating composition must be selected within the range corresponding to RuO_2 and MnO_2 in a mole ratio from 1:1 to 1:9, and preferably between 1:2 and 1:4, in order to be able to maintain a low, practically constant oxygen potential and to ensure a high anode life under oxygen evolving conditions.

The proportion of manganese in the oxide coating may moreover be considerably increased within said range, without notably increasing the oxygen potential, while the anode life under oxygen evolving conditions may be significantly increased when the proportion of manganese in the oxide coating is increased towards its upper limit within said range.

It has also been established that the number of oxide layers applied according to the invention is important with regard to the anode life. It must be more particularly selected from the range between 6 and 35 layers, preferably between about 10 and about 20 layers, namely according to the selected coating composition and the total ruthenium loading applied in each case. This loading lies within the range from 4 to 20, preferably about 6 to about 12 grams of ruthenium per square meter of the anode base surface. Said loading should be selected from case to case according to the compostion of the coating produced according to the invention.

Thus, it has been established that stable oxide coatings with a high proportion of manganese may be advantageously produced in the composition range according to the invention by applying a relatively low ruthenium loading of 4 to 8 g/m^2 in 10 to 20 layers. On the other hand, oxide coatings with a minimum proportion of manganese, corresponding to the 1:1 mole ratio of the composition range according to the invention, should be produced with a higher ruthenium loading of 8 to 20 g/m^2 which is applied in a relatively large number of layers, namely 10 to 20 layers, or more, in order to provide an adequate anode life.

The ruthenium and manganese compounds contained in the coating solution which is applied according to the invention should be completely dissolved in the in order to ensure a uniform, ultrafine mixture of ruthenium and manganese throughout the oxide coating obtained by thermal conversion. The invention was successfully carried out with ruthenium chloride and manganese nitrate or manganese oxalate.

Coating solutions were successfully applied according to the invention which comprisied an aqueous solvent or an organic solvent, more particularly ethanol, or butanol.

Concentrated hydrochloric acid was also included in an amount corresponding to about 4% - 15% by weight of the coating solution, which likewise provided a good coating.

The thermal decomposition temperatures of the ruthenium and manganese compounds used to produce an oxide coating according to the invention differ considerably, so that they must be subjected to heat treatment at a temperature which is specially selected so as to be suitable to ensure their simultaneous conversion into a satisfactory, uniform oxide coating. It has been experimentally established that heat treatment at a temperature of about 400°C is essential in order to to ensure a satisfactory coating according to the invention, whereas it was found that significantly higher or lower temperatures, above 420°C, or below 380°C, does not provide a satisfactory coating.

The following examples illustrate different modes of carrying out the invention.

Example 1

Titanium anodes comprising a catalytic Ru-Mn oxide coating with a composition corresponding to a 50 RuO_2/50 MnO_2 mole ratio were manufactured in the following manner.

A homogeneous coating solution of ruthenium chloride and manganese nitrate dissolved in water in a mole ratio 1:1 was prepared with the following composition by weight:

10.5 % $RuCl_3$aq.(40% Ru); 10.5 % $Mn(NO_3)_2.4\ H_2O$; 4.7 % HCl (10 N); 74.3 % H_2O.

Titanium coupons (100x20x1mm) were pretreated by sandblasting and etching in boiling 15% HCl for 30 minutes.

The coating solution was successively applied with a brush in 10 layers to the pretreated titanium coupons. Each applied layer of solution was dried for 5 minutes in air at 100°C and the resulting dried layer was heat treated at 400°C for 10 minutes in a stream of air, whereby the metal salts are thermally decomposed and converted to oxide.

The oxide coating thus produced in 10 layers with a molar composition corresponding to 50 RuO_2/50 MnO_2 contained ruthenium in a specific amount or loading per unit area of the titanium substrate surface corresponding to 8 g/m^2 .

One anode (S46) with a coating thus produced in 10 layers with a total loading of Ru = 8 g/m^2 was subjected to an accelerated life test by operating it at 7500 A/m^2 as an oxygen evolving anode in 150 gpl H_2SO_4, while the anode operating potential was monitored until it exhibited a steep rise indicating anode failure. The accelerated test lifetime of this anode (S46) was 90 hours.

Another anode (S28) was similarly produced , except that manganese oxalate was used in this case to replace manganese nitrate previously used. This anode (S28) exhibited an accelerated test lifetime of 85 hours at 7500 A/m^2..

Example 2

Titanium anodes with a catalytic Ru-Mn-Co oxide coating were prepared under the conditions described in Example 1, except that a solution of ruthenium chloride, manganese nitrate and cobalt nitrate dissolved in water was prepared with the following composition by weight:
10% $RuCl_3$ aq.(40% Ru); 10% $Mn(NO_3)_2.4H_2O$;
2.6% $Co(NO_3)_2.6H_2O$; 12% HCl(10N); 65.4% H_2O.
A titanium coupon was pretreated as in Example 1, coated by applying this solution in 10 layers, drying and heat treating as described in Example 1, so as to produce an oxide coating in 10 layers with a total loading of Ru = 8 g/m^2 and an overall composition corresponding to RuO_2, MnO_2, and Co-oxide in a mole ratio of 45:45:10.
The coated anode (S37-I) thus obtained was tested as an oxygen evolving anode operating at 500 A/m^2 in 150 gpl H_2SO_4, had an initial oxygen potential of 1.50 V vs.NHE, and was still operating with an oxygen potential of 1.70 V vs. NHE after 20 months. A similar anode (S37-I) was subjected to the accelerated life test described in Example 1 and its accelerated test life was 90 hours at 7500 A/m^2.
Other anodes (S37-II) were prepared under similar conditions, except that the coating solution used in this case had the following composition by weight: 10% $RuCl_3$ aq.(40% Ru); 8.8% $Mn(NO_3)_2O$; 1.2% $Co(NO_3)_2.6\ H_2O$;
12.2% HCl(10N); 67.8% H_2O. The coated anodes produced from this solution had an oxide coating with a loading of Ru = 8 g/m^2 and an overall composition corresponding to RuO_2, MnO_2, and Co-oxide in a mole ratio of 50:45:5.
One such anode was operated at 500 A/m^2 in 150 gpl H_2SO_4, had an initial oxygen potential of 1.60 V vs. NHE (Normal Hydrogen Electrode), and failed after 13 months at 500 A/m^2. A similar anode (S37-II) exhibited an accelerated test life of 40 hours at 7500 A/m^2 in 150 gpl H_2SO_4.

Example 3

Titanium anodes with a catalytic Ru-Mn oxide coating containing dispersed anatase TiO_2 powder of submicronic particle size, were produced as described in Example 1, in the following manner.

The coating solution used in this case comprised ruthenium chloride and manganese nitrate dissolved in a 50 Ru/50 Mn mole ratio in n-butyl alcohol, further contained anatase TiO_2 powder uniformly dispersed throughout the solution, and had the following composition by weight:

12.6% $RuCl_3$ aq.(40% Ru); 12.2% $Mn(NO_3)_2.4\ H_2O$;

3.9% dispersed anatase TiO_2 powder; 71.3% BuOH.

This solution was successively applied in 7 layers and converted to oxide under the conditions described in Example 1, so as to produce a catalytic Ru-Mn oxide coating containing uniformly dispersed anatase TiO_2 powder, applied in 7 layers with a loading of Ru = 15 g/m^2 and an overall composition corresponding to RuO_2, MnO_2, and TiO_2 in a mole ratio of 1:1:1.

One anode (S141) thus produced in 7 layers with a total loading of Ru = 15 g/m^2, was subjected to an accelerated life test as described in Example 1 and exhibited a test life of 175 hours at 7500 A/m^2 in 150 gpl H_2SO_4.

Another anode (S141) produced in exactly the same manner was tested as an oxygen-evolving anode operating at 500 A/m^2 in 150 gpl H_2SO_4, had an initial oxygen potential of 1.53 V vs. NHE, and operated at 1.63 V vs. NHE after 23 months.

A second set of anodes (S142) was prepared by applying 8 layers of the same coating solution, which was dried, and thermally converted, as described in Example 1, so as to produce an oxide coating applied in in this case in 8 layers with a total loading of Ru = 8 g/m^2, and with the same overall composition corresponding to RuO_2 and MnO_2 in a mole ratio of 1:1.

One anode (S142) of this second set was tested at 500 A/m^2 in 150 gpl H_2SO_4, and operated with an oxygen potential of 1.57 V vs. NHE after 7000 hours (292 days) under these test conditions.

Another anode (S142) of this second set exhibited an accelerated test life in 150 gpl H_2SO_4 of 79 hours at 7500 A/m^2 .

Further anodes were prepared in a similar manner from two coating solutions, so as to produce oxide coatings with a loading of Ru = 8 g/m^2 and overall compositions corresponding to RuO_2, MnO_2, and TiO_2 (powder) in a mole ratio of 1:1:3 and 2:2:1,respectively.

An anode (S143) with a coating composition corresponding to: 1 RuO_2:1 MnO_2:3 TiO_2(powder) exhibited an accelerated test life of 68 hours at 7500 A/m^2 in 150 gpl H_2SO_4.

Another anode (S144) with a coating corresponding to : 2 RuO_2:2 MnO_2:1 TiO_2 (powder) had an accelerated test life of 80 hours at 7500 A/m^2.

Example 4

Titanium anodes with a catalytic Ru-Mn oxide coating containing dispersed titanium metal powder with a particle size of 20 to 40 microns, were produced as follows.

The coating solution used in this case comprised ruthenium chloride and manganese nitrate dissolved in a 1:1 mole ratio in water, further contained titanium metal powder uniformly dispersed throughout the solution, and had the following overall composition by weight: 10.3% $RuCl_3$ aq.(40% Ru); 10.1% $Mn(NO_3)_2.4H_2O$; 2% dispersed Ti powder ; 4.6% HCl (10N); 73% H_2O.

This solution was applied in 7 layers and converted to oxide as described in Example 1, so as to produce an oxide coating containing uniformly dispersed titanium powder, which was applied in 7 layers with a total loading of Ru = 8.4g/m^2 and an overall composition corresponding to a mole ratio of 38 RuO_2:38 MnO_2:24 Ti (powder).

An anode (S48), with a coating thus applied in 7 layers with Ru = 8.4g/m^2, was subjected to an accelerated life test as described in Example 1 and exhibited an accelerated test life in 150 gpl H_2SO_4 of 134 hours at 7500 A/m^2 .

It may thus be seen that the addition of dispersed titanium powder to the oxide coating of this anode (S48) with Ru = 8.4 g/m^2 and a composition corresponding to $RuO_2$and MnO_2 in a mole ratio of 1:1, provides an anode with improved stability to oxygen evolution. This improvemenyt is apparent from the accelerated test life of 137 hours at 7500 A/m^2 obtained with this anode (S48), which is significantly higher than the 90 hours obtained with the anode (S46) in Example 1, which had nearly the same loading of Ru = 8 g/m^2, and a coating composition with the same 1:1 mole ratio of RuO_2:MnO_2 (but containing no dispersed Ti).

A similar improvement due to the addition of dispersed titanium powder may be observed by comparing this anode (S48) having an accelerated test life of 137 hours for with the with the anodes (S142), (S143), and (S144) of Example 3, which had an accelerated test life of 70-80 hours obtained with nearly the same loading of Ru = 8 g/m^2 and a coating composition with the same 1:1 mole ratio of RuO_2:MnO_2 (but containing dispersed anatase TiO_2).

This observed significant improvement of the anode stabilty due to the addition of dispersed titanium powder can not be exactly explained, but might possibly be attributed to a favorable effect of the dispersed titanium powder on the surface of the Ru-Mn oxide coating, or to a favorable chemical interaction between the dispersed titanium powder and the Ru-Mn oxide during its formation, or possibly both together.

Example 5

Titanium anodes comprising a catalytic Ru-Mn oxide coating with an overall composition corresponding to RuO_2 and MnO_2 in a mole ratio of 30:70 were manufactured in the following manner.

A coating solution of ruthenium chloride and manganese nitrate dissolved in a mole ratio of 30:70 in 1-butyl alcohol was prepared with the following composition by weight: 11.1% $RuCl_3$aq.(40% Ru); 25.8% $Mn(NO_3)_2.4H_2O$; 63.1% butanol.

Titanium coupons (100x20x1mm) were pretreated by sandblasting, treating in 1,1,1-trichlorethane for 10 minutes, and etching in oxalic acid at 80°C for 6 hours.

The coating solution was successively applied with a brush in 20 layers to the pretreated titanium coupons, each applied layer of solution was dried for 10 minutes in air at 120°C, and each dried layer was heat treated at 400°C for 10 minutes in a stream of air, whereby the metal salts are thermally decomposed and converted to oxide. The resulting oxide coating, with a 30 RuO_2:70 MnO_2 composition applied in 20 layers, had a loading of Ru = 8 g/m^2.

One anode (B2) with a coating thus produced in 20 layers with Ru = 8g/m^2 exhibited an accelerated test life of 176 hours at 7500 A/m^2 in 150 gpl H_2SO_4.

Another anode (B1) was similarly produced, but by applying 13 layers of the same coating solution, so as to produce a coating with a loading of Ru=6 g/m^2, and it exhibited an accelerated test life of 142 hours at 7500 A/m^2.

Another anode (B4) was similarly produced, but by applying 30 layers of the same solution, so as to obtain a coating with a loading of Ru = 12 g/m^2, and it exhibited an accelerated test life of 137 hours at 7500 A/m^2 in 150 gpl H_2SO_4.

A comparative titanium anode (Q42) with a catalytic Ru-oxide coating containing dispersed beta-MnO_2 powder with a mean particle size of 40 microns, was produced in the manner described in Example 1, but by successsively applying five Ru-oxide layers having a total loading of Ru = 8 g/m^2, and containing dispersed MnO_2 powder in an amount corresponding to the same overall coating composition as the anodes B1, B2, B4 above, namely 30% RuO_2 and 70% MnO_2 (applied as a dispersed, preformed powder in this comparative anode Q42). The coating solution used in this case comprised dissolved ruthenium chloride and dispersed MnO_2 powder, and had the following composition by weight: 12.7 % $RuCl_3$ aq.(40 % Ru); 10.0 % dispersed beta-MnO_2 powder (mean size 40 microns); 5.3 % HCl (10 N); 72 % n-butyl alcohol.

This solution was applied in 5 layers and converted to oxide as described in Example 1, so as to produce a ruthenium oxide coating containing dispersed beta-MnO_2 powder, formed in 5 layers with a total loading of Ru = 8 g/m^2.

The comparative anode (Q42), thus obtained with a coating applied in 5 layers with a composition corresponding to 30 RuO_2 and 70 MnO_2(powder) and a loading of Ru = 8 g/m^2, exhibited an accelerated test life of 60 hours at 7500A/m^2.

It may thus be seen that this comparative anode (Q42) having a coating with the same overall composition as B2, but containing MnO_2 powder which is preformed and dispersed, exihibits an accelerated test life of 60 hours at 7500A/m^2, while anode B2 with the same loading of Ru = 8 g/m^2 and the same overall coating composition, but with Ru-Mn oxide formed in situ, exhibited an accelerated test life at 7500 A/m^2 of 176 hours, which is about 3 times higher.

This accelerated test life of 176 hours, which was achieved by the anode (B2) having a Ru-Mn oxide coating with a loading of Ru = 8 g/m^2 and an overall composition corresponding to RuO_2 and MnO_2 in a mole ratio of 30:70, is moreover about twice as high as the 85-90 hours obtained with the anodes

(S46) and (S48) of Example 1 which had a Ru-Mn oxide coating having the same loading of Ru = 8 g/m^2, but with an overall composition corresponding to RuO_2 and MnO_2 in a mole ratio of 1:1, which is at the lower limit of the proportion of ruthenium applied in the method according to the present invention.

This comparison shows the particular significance of manufacturing a Ru-Mn oxide coating according to the method of the present invention, namely by applying a major amount of manganese oxide which is simultaneously formed in situ with a minor amount of ruthenium oxide.

Example 6

Titanium anodes comprising a catalytic Ru-Mn oxide coating with a composition corresponding to RuO_2 and MnO_2 in a mole ratio of 14:86 were manufactured in the following manner.

A coating solution containing ruthenium chloride and manganese nitrate dissolved in a mole ratio 1:6 in 1-butyl alcohol was prepared with the composition by weight:

8.3% $RuCl_3$aq.(40% Ru); 48.1% $Mn(NO_3)_2.4\ H_2O$;

43.6% butanol.

Titanium coupons (100x20x1mm) were pretreated by sandblasting treating in 1,1,1-trichlorethane for 10 minutes and etching in oxalic acid at 80°C for 6 hours. The coating solution was successively applied with a brush in 22 layers to the pretreated titanium coupons, each applied layer of solution was dried for 10 minutes in air at 120°C, and the resulting dried layer was heat treated at 400°C for 10 minutes in a stream of air, whereby the metal salts are thermally decomposed and converted to oxide. The oxide coating thus applied in 22 layers had a total loading of Ru = 8 g/m^2 and an overall composition corresponding to 14 RuO_2:86 MnO_2 .

One anode (E1) with a coating thus produced in 22 layers with Ru = 8 g/m^2 exhibited an accelerated test life of 200 hours at 7500 A/m^2 in 150 gpl H_2SO_4.

Another anode (E2) was produced by applying 16 layers of the same solution, with a total loading of Ru = 6 g/m^2, and exhibited an accelerated test life of 182 hours at 7500Am/^{2}.

A further anode (E3) was produced by applying 28 layers of said solution, with a total loading of Ru = 10 gm/^{2}, and exhibited an accelerated test life of 160 hours.

Another anode (E4) was produced by applying 33 layers of said solution with a total loading of Ru = 12 g/m^2, and exhibited an accelerated test life of 193 hours.

As may be seen from the above accelerated test results, such anodes with a high MnO_2/RuO_2 mole ratio of 86:14 (about 6:1) exhibit an accelerated test life of 182 to 200 hours in the case of anodes (E1) and (E2) having a Ru-Mn oxide coating applied in 16-22 layers with a loading of Ru = 6 to 8 g/m^2. On the other hand, anodes (E3) and (E4) with an increased number of applied coating layers (28-33) and a higher ruthenium loading (Ru = 10-12 g/m^2) provide no significant improvement over the anodes (E1) and (E2) with in fewer applied layers and a lower ruthenium loading.

Other anodes were similarly produced in 18 layers with a total loading Ru = 8 g/m^2, were similarly tested but at a lower current density, and exhibited an accelerated test life in H_2SO_4 corresponding respectively to:

Anode (4A): 520 hours at 3750 A/m^2
Anode (3A): 1760 hours at 1875 A/m^2
Anode (2A): 8160 hours at 940 A/m^2.

It may be noted that these accelerated tests are caried out at a considerably higher current density than is normally required for most industrial applications of oxygen evolving anodes. The accelerated test life measured in the present tests should thus correspond to a considerably longer service life during normal operation at a lower anode current density, such as for example 200 A/m^2, which is typically applied in processes for electrowinning copper from a sulphate electrolyte.

Example 7

Titanium anodes comprising a catalytic Ru-Mn oxide coating with a composition corresponding to RuO_2 and MnO_2 in a mole ratio of 1:4 were manufactured in the following manner. A coating solution comprising ruthenium chloride and manganese nitrate dissolved in a mole ratio 1:4 in 1-butyl alcohol was prepared with the composition by weight: 9.5% $RuCl_3$aq.(40% Ru); 36.8% $Mn(NO_3)_2.4H_2O$; 53.7% butanol. This coating solution was succesively applied, dried, and converted to an oxide coating under the conditions previously described.

One anode (C2), thus obtained with a catalytic Ru-Mn oxide coating applied in 20 layers with a total loading of Ru = 8 g/m^2 and a composition corresponding to 20 RuO_2:80 MnO_2, exhibited an accelerated test life of 175 hours at 7500 A/m^2 in 150 gpl H_2SO_4.

Another such anode (C1), similarly produced but by applying 16 layers of the same solution with a total loading of Ru = 12 g/m^2, exhibited an accelerated test life of 135 hours at 7500 A/m^2.

A further such anode (C3), similarly produced but by applying 21 layers of the same solution with a total loading of Ru = 10 g/m^2, exhibited an accelerated test life of 187 hours at 7500 A/m^2.

Another anode (C4), similarly produced but by applying 30 layers of the same solution with a total loading of Ru = 12 g/m^2, exhibited an accelerated test life of 126 hours at 7500A/m^2.

As may be seen from the above accelerated test results, such anodes with a high MnO_2/RuO_2 mole ratio of 4:1 exhibit an accelerated test life of 175-187 hours in the case of anodes (C2) and (C3) having a Ru-Mn oxide coating applied in 20-21 layers with a loading of Ru = 8 to 10 g/m^2. On the other hand, anodes (C4) and (C1) with a higher total loading of Ru = 12 g/m^2 applied respectively in 16 and 30 coating layers exhibit an accelerated test life of 126-137 hours and provide no improvement over the anodes (C2) and (C3) with an accelerated test life of 175-187 hours which is about 40% higher than for (C4) and (C1).
It may also be seen from the above test results that anode (C4) with a loading of Ru = 12 g/m^2 applied in 30 layers has an accelerated test life of 126 hours, and thus shows no significant improvement with respect to the test life of 135 hours of anode (C1) with the same coating composition and the same loading, but applied in 16 layers. Thus, an increase of the number of coating layers applied from 16 up to 30 does not improvement the stability of such an anode.

EXAMPLE 8

Titanium anodes with oxide coatings comprising different amounts of ruthenium and/or manganese were prepared and tested in the following manner.
Titanium coupons (100x20x1mm) were pretreated by sandblasting, treating in 1,1,1-trichlorethane for 10 minutes, and etching in oxalic acid at 80°C for 6 hours.
A comparative anode Ru100 with a Ru-oxide coating (100 % RuO_2) was prepared by:
(a) successively applying with a brush to a pretreated titanium coupon 9 layers of a coating solution with the following composition by weight: 0.8 g $RuCl_3$aq.(40% Ru); 2.4 g ethanol; and 0.25 ml HCl (10N); (b) drying each applied

layer of solution for 15 minutes in air at 120°C; and (c) heat treating each dried layer at 400°C for 10 minutes in a stream of air, whereby the metal salts are thermally decomposed and converted to oxide.

This comparative anode Ru100 with a Ru-oxide coating applied in 9 layers, with a loading of Ru = 8 g/m^2, was tested as an oxygen evolving anode in 150 gpl H_2SO_4, exhibited an oxygen potential of 1.56 V vs. NHE at 500 A/m^2, and had an accelerated test life of 3.5 hours at 7500A/m^2.

An anode Ru90 was similarly provided with a Ru-Mn oxide coating having a composition corresponding to a RuO_2: MnO_2 mole ratio of 9:1 by applying in this case 9 layers of a coating solution with the composition by weight: 0.926 g $RuCl_3$aq.(40% Ru); 0.103 g $Mn(NO_3)_2.4H_2O$; 5.5 g ethanol; and 0.25 ml HCl (10N), and then drying and heat treating each applied layer in the same manner as described in steps (b) and (c) above.

This anode Ru90 was thus provided with a 90 RuO_2/10 MnO_2 coating applied in 9 layers with Ru = 8.1 g/m^2, was similarly tested in 150 gpl H_2SO_4, exhibited an oxygen potential of 1.53 V vs. NHE at 500 A/m^2, and had an accelerated test life of 9.8 hours at 7500 A/m^2.

An anode M5 was similarly provided with an Ru-Mn oxide coating having a composition corresponding to a 80 RuO_2:20 MnO_2 mole ratio by applying in this case 7 layers of a coating solution with the composition by weight: 0.721 g $RuCl_3$aq.(40% Ru); 0.180 g $Mn(NO_3)_2.4H_2O$; 5.9 g ethanol; and 0.25 ml HCl (10N), and then drying and heat treating each applied layer as described in steps (b) and (c) above.

This anode M5 was thus provided with a 80 RuO_2/20 MnO_2 coating applied in 7 layers with Ru = 8 g/m^2, was similarly tested in 150 gpl H_2SO_4, exhibited an oxygen potential of 1.53 V vs. NHE at 500 A/m^2, and had an accelerated test life of 10 hours at 7500 A/m^2.

An anode M8 was similarly provided with a Ru-Mn oxide coating having a composition corresponding to a 50 RuO_2:50 MnO_2 mole ratio, but by applying in this case 8 layers of a coating solution with the composition by weight: 0.684 g $RuCl_3$aq.(40% Ru); 0.680 g $Mn(NO_3)_2.4H_2O$; 3.6 g ethanol; and 0.25 ml HCl (10 N), and then drying and heat treating each layer as described in (b) and (c) above. This anode M8 was thus provided with a 50 RuO_2/50 MnO_2 coating applied in 8 layers with Ru = 8 g/m^2, was similarly tested in 150 gpl H_2SO_4, exhibited an oxygen potential of 1.56 V vs. NHE at 500 A/m^2, and had an accelerated test life of 55 hours at 7500 A/m^2.

An anode M4 was similarly provided with a Ru-Mn oxide coating having a composition corresponding to a 30 RuO_2:70 MnO_2 mole ratio, but by applying in this case 7 layers of a coating solution with the composition by weight: 1.074 g $RuCl_3$aq.(40 % Ru); 2.419 g $Mn(NO_3)_2.4H_2O$; 3.6 g ethanol; and 0.25 ml HCl (10N), and then drying and heat treating each layer as described in (b) and (c) above. This anode M4 was thus provided with a 30 RuO_2/70 MnO_2 coating applied in 7 layers with Ru = 8 g/m^2, was similarly tested in 150 gpl H_2SO_4, exhibited an oxygen potential of 1.55 V vs. NHE at 500 A/m^2, and had an accelerated test life of 115 hours at 7500 A/m^2.

An anode M13 was similarly provided with a Ru-Mn oxide coating having a composition corresponding to a 14 RuO_2:86 MnO_2 mole ratio, but by applying in this case 11 layers of a coating solution with the composition by weight: 0.537 g $RuCl_3$aq.(40 % Ru); 3.127 g $Mn(NO_3)_2.4H_2O$; 2.835 g ethanol; and 0.25 ml HCl (10N), and then drying and heat treating each layer as described in (b) and (c) above. This anode M13 was thus provided with a 14 RuO_2/86 MnO_2 coating applied in 11 layers with Ru = 8 g/m^2, was similarly tested in 150 gpl H_2SO_4, exhibited an oxygen potential of 1.57 V vs. NHE at 500 A/m^2, and had an accelerated test life of 200 hours at 7500 A/m^2 .

Another comparative anode Mn100 was similarly provided with a Mn-oxide coating (MnO_2), but by applying in this case 11 layers of a solution with the composition by weight: 1.12 g $Mn(NO_3)_2.4H_2O$; and 10 g ethanol, then drying as described above in (b), and heat treating each dried layer at 320°C in a stream of air for 10 minutes (conditions considered suitable to produce a MnO_2 coating by thermal decomposition). The total manganese loading of the resulting oxide coating (100 % MnO_2) was Mn = 26 g/m^2 in this case (i.e. the same as for anode M13).

This anode Mn100 was thus provided with a MnO_2 coating applied in 11 layers with Mn = 26 g/m^2, was similarly tested in 150 gpl H_2SO_4, exhibited an oxygen potential above 3 V vs. NHE at 500 A/m^2, and failed immediately in the accelerated test at 7500 A/m^2.

It may thus be seen from the above test results that the anodes M8, M4, and M13, which were produced with a Ru-Mn oxide coating by the method according to the invention, show no significant increase of the oxygen potential, while at the same time exhibiting a several times higher anode life under oxygen evolving conditions, when the proportion of ruthenium in the coating composition is decreased within the range of the invention, coresponding to RuO_2 and MnO_2 in a mole ratio from 1:1 to 1:9.

It may further be noted that the anode M4 described above and anode (B2) described in Example 5 were both produced according to the invention with the same coating composition corresponding to 30 RuO_2/70 MnO_2 and the same loading of Ru = 8 g/m^2. This anode M4, with a coating applied in 7 layers exhibited an accelerated test life of 115 hours, whereas the anode (B2) with a similar coating applied in 20 layers, exhibited an accelerated test life of 176 hours, which is significantly higher. Thus, an increase of the number of coating layers applied from 7 to 20 layers in such anodes with a coating composition corresponding to

30 RuO_2/70 MnO_2 and a loading of Ru = 8 g/m^2, provides a significant increase of the anode life under oxygen evolving conditions, as may be seen from the corresponding increase of the accelerated test life from 115 to 176 hours. Anode M13 described above and anode (E1) described in Example 6 were morevover both produced according to the invention, with the same coating composition corresponding to 14 RuO_2/86 MnO_2 and the same loading of Ru = 8 g/m^2. This anode M13, with a coating applied in 11 layers, exhibited an accelerated test life of 200 hours, while anode (E1) with a similar coating applied in 22 layers, exhibited the same accelerated test life of 200 hours. Thus, an increase of the number of coating layers from 11 to 22 layers applied with a loading of Ru = 8 g/m^2, provides no modification of the anode life under oxygen evolving conditions in the case of such anodes with a coating composition corresponding to 14 RuO_2/86 MnO_2, as may be seen from the same accelerated test life of 200 hours in both cases.

TECHNICAL APPLICABILITY

The invention may be used for the production of dimensionally stable anodes for industrial applications of catalytic oxygen evolving anodes where restriction of the anode costs is an essential requirement. Anodes produced by the invention may be more particularly applied in processes for electrowinning metals such as copper and zinc from sulphate electrolytes.

CLAIMS

1. A method of manufacturing a dimensionally stable, oxygen evolving anode which comprises an anode base of film-forming metal with a catalytic oxide coating containing ruthenium, characterized by the steps of :

a) applying to the anode base successive layers of a coating solution containing ruthenium and manganese compounds in concentrations corresponding to a predetermined mole ratio of ruthenium dioxide to manganese dioxide selected from the range between 1:1 and 1:9;

b) drying each layer of the coating solution applied in step a), so as to obtain a substantially dry layer comprising a uniform mixture of the ruthenium and manganese compounds in said predetermined ratio;

c) subjecting the resulting dry layer to heat treatment which is effected in 5 to 15 minutes in an oxidizing atmosphere at a temperature of about 400°C , so as to convert said compounds into a uniform oxide layer;

d) carrying out steps a), b) and c) repeatedly so as to successively form 6 to 35 oxide layers upon one another, the number of said oxide layers being selected so as to gradually build up a catalytic oxide coating containing a predetermined amount of ruthenium per unit area of the anode base, corresponding to a ruthenium loading selected from the range from 4 g/m^2 to 20 g/m^2.

2. The method of claim 1, characterized in that the anode base consists essentially of titanium or titanium alloy.

3. The method of claim 1, characterized in that said catalytic coating is made by successively forming 10 to 20 of said oxide layers according to a), b) and c).

4. The method of claim 1 or 2, characterized in that said mole ratio is selected from the range between 1 Ru/2 Mn and 1 Ru/6 Mn and that said ruthenium loading is selected from the range between 6 and 12 g/m^2.

5. The method of claim 4, characterized in that said mole ratio is selected from the range between 1 Ru/4 Mn and 1 Ru/6 Mn.

6. The method of claim 1 for manufacturing an anode intended for use in a process for metal electrowinning from an acid electrolyte further containing manganese as an impurity, characterized in that said mole ratio is selected from the range between 1 Ru/1 Mn and 1 Ru/3 Mn.

7. The method of claim 1, characterized in that said coating solution contains concentrated hydrochloric acid in an amount corresponding to from about 4 to 15 percent by weight of said solution.

8. The method of claim 1, characterized in that said coating comprises ethanol or butanol as an organic solvent.

9. The method of claim 1, characterized in that titanium powder having a prtcle size smaller than 40 microns is uniformly dispersed in said coating solution in an amount which is selected so that said catalytic coating contains the titanium powder in an amount corresponding to a titanium loading of at most 10 g/m^2.

10. The method of claim 1, characterized in that titanium oxide powder consisting of particles of submicronic size is finely dispersed in said coating solution.

11. A dimensionally stable anode produced by the method of claim 1 or any of claims 2 to 10.

European Patent Office

EUROPEAN SEARCH REPORT

0135475

Application number

EP 84 81 0391

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	EP-A-0 046 448 (DIAMOND SHAMROCK) * Page 8, lines 3-36; page 9, lines 1-17; page 18, line 35; page 19, lines 1-7; table 3 last example * ---	1,2,11
Y	FR-A-2 479 272 (KUBASOV) * Page 10, example 7; page 3, lines 14-37; page 7, lines 6-11 * ---	1,2,3
A	EP-A-0 013 572 (DIAMOND SHAMROCK) ---	
Y	FR-A-2 083 493 (DIAMOND SHAMROCK) * Page 4, lines 15-28; page 8, example 3; page 10, claims * -----	1,2

CLASSIFICATION OF THE APPLICATION (Int Cl.4)

C 25 B 11/06
C 25 C 7/02

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 25 B 11
C 25 C 7

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20-11-1984	GROSEILLER PH.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document